6. ENVIRONMENTAL CONCENTRATIONS

6.1 BACKGROUND, PURPOSE, AND SCOPE

This chapter summarizes the concentrations of particulate matter over the United States, including the spatial, temporal, size and chemical aspects. The information needs for assessing the major aerosol effects of concern are summarized in Table 6-1. The general approach followed in preparing this chapter was to organize, evaluate, and summarize the existing large scale aerosol data sets over the United States. Emphasis was placed on complete national coverage as well as the fusion and reconciliation of multiple data sets.

Space is the main organizing dimension used to structure this chapter. Aerosol concentration data are presented on global, continental, national, regional, and sub-regional/urban scales. Within each spatial domain, the spatial-temporal structure, size, and chemical composition are presented. An overview of the pattern analysis methods is given in the remainder of Section 6.1. The presentation of aerosol patterns begins from the global and continental perspective (Section 6.2). Next, nationwide aerosol patterns (Section 6.3) derived from nonurban and urban PM_{10} and $PM_{2.5}$ monitoring networks are examined. Section 6.3 also includes a discussion of various measures of background $PM_{2.5}$ and PM_{10}. In Section 6.4 the aerosol characteristics over seven subregions of the conterminous United States are examined in more detail. The 10-year trends, seasonal patterns, relationships between $PM_{2.5}$ and PM_{10}, and fine particle chemical composition are examined for each region. Section 6.5 focuses further on the subregional and urban-scale aerosol pattern over representative areas of the United States. Section 6.6 presents more detailed information on the chemical composition of the aerosol from a number of intensive field studies. Section 6.7 deals with measurements of fine particle acidity. Section 6.8 focuses on the concentration of ultrafine particles and Section 6.9 on the chemical composition of ultrafine particles. Section 6.10 examines trends and relationships for $PM_{2.5}$, $PM_{(10-2.5)}$, and PM_{10} in data bases having long term data on both components.

Aerosol concentration data for the United States have been reported by many aerosol researchers over the past decade. This chapter draws heavily on the contribution, of research groups that have produced data, reports, and analyses of nonurban data. However, their maps, charts, and computations have been re-done for consistency with urban data reports.

6.1.1   Dimensionality and Structuring of the Aerosol Data Space

Aerosol concentration patterns contain endless detail and complexity in space, time, size, and chemical composition. Aerosol samples from the conterminous United States reveal the coexistence of sulfates, hydrogen ions, ammonium, organic carbon (OC), nitrates, elemental carbon (EC [soot]), soil dust, sea salt, and trace metals. This chemically rich aerosol mixture arises from the multiplicity of contributing aerosol sources, each having a unique chemical mixture for the primary aerosol at the time of emission. The primary aerosol chemistry is further enriched by the addition of species during atmospheric chemical processes. Finally, the immensely effective mixing ability of the lower troposphere stirs these primary and secondary particles into a mixed batch with varying degrees of homogeneity, depending on location and time.

A major consideration in structuring the aerosol pattern analysis is that it has to be consistent with the physical and chemical processes that determine the concentrations of the aerosol. The concentration of particulate matter (C), at any given location and time is determined by the combined interaction of emissions (E), dilution (D), and chemical transformation and removal processes (T),expressed as:

$$C = f(D,T,E)$$

Dilution, transformation/removal, and emissions are generic operators and can, in principle, be determined from suitable measurements and models. However, for consideration of aerosol pattern analysis it is sufficient to recognize and separate these three major causal factors influencing the aerosol concentration pattern.

It is convenient to categorize the highly variable aerosol signal along the following major dimensions: space, time, size and chemical composition. The dependence of concentration on space and time is common to all pollutants. However, both the distribution with respect to particle size as well as the chemical distribution within a given size range constitute unique dimensions of particulate matter that are not present for other pollutants. The concentrations of single-compound gaseous pollutants can be fully characterized by their spatial and temporal pattern. This classification by dimensions is consistent with the size-chemical composition distribution function introduced by Friedlander (1977). It could be said that particulate matter is

a composite of hundreds of different substances exhibiting a high degree of spatial and temporal variability.

6.1.2   Spatial Pattern and Scales

The spatial dimension covers the geographic scale and pattern of aerosols. Based on consideration of emissions, meteorology, and political boundaries, the spatial dimension can be broken into global, national, regional-synoptic, meso, urban, and local scales. Some of the characteristics of these spatial scales are illustrated in Table 6-1.

TABLE 6-1. SPATIAL REGIONS AND SCALES

Global	National	Regional	Meso	Urban	Local
Continent	Country	Multi-state	State	County	City center
10,000 - 50,000 km	5,000 - 10,000 km	1,000 - 5,000 km	100 - 1,000 km	10 - 100 km	1 - 10 km

6.1.3   Temporal Pattern and Scales

The time dimension of aerosols extends over at least six different scales (Figure 6-1). A significant, unique feature of the temporal domain is the existence of periodicities. The secular time scale extends over several decades or centuries. Given climatic and chemical stability of the atmosphere the main causes of secular concentration trends are changes in anthropogenic emissions. Emissions, atmospheric dilution, as well as chemical/removal processes, can be influenced by the seasonal cycle. The synoptic scale covers the duration of
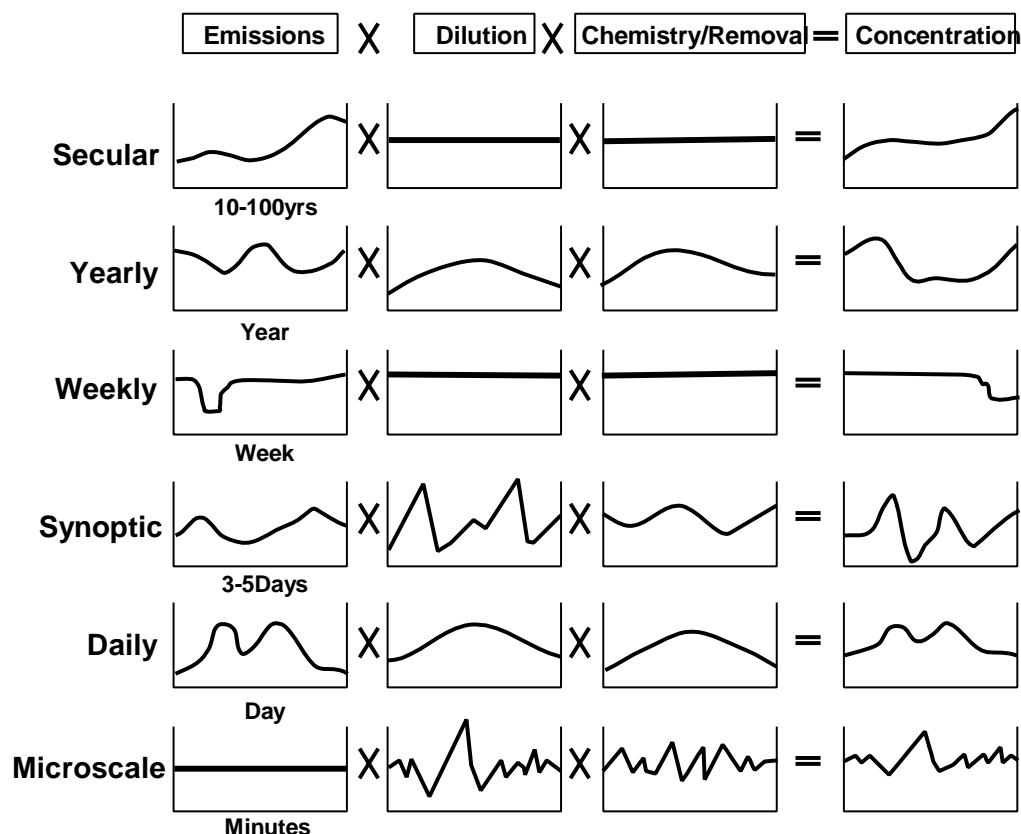
Figure 6-1.   Time scales for particle emissions.

synoptic meteorological events (3-5 days). Its role is primarily reflected in dilution and chemical/removal processes. The daily cycle strongly influences the emissions, dilution, and chemical/removal processes. Microscale defines variation of the order of an hour caused by short-term atmospheric phenomena. In the analysis that follows we will emphasize secular trends and yearly cycles, with some consideration of daily aerosol pattern. The microscale patterns will be largely ignored.

6.1.4   Space-Time Relationships

The spatial and time scales of aerosol pattern are linked by the atmospheric residence time of particles. Short residence times restrict the aerosol to a short transport distance from a source, causing strong spatial and temporal gradients. Longer residence times yield more
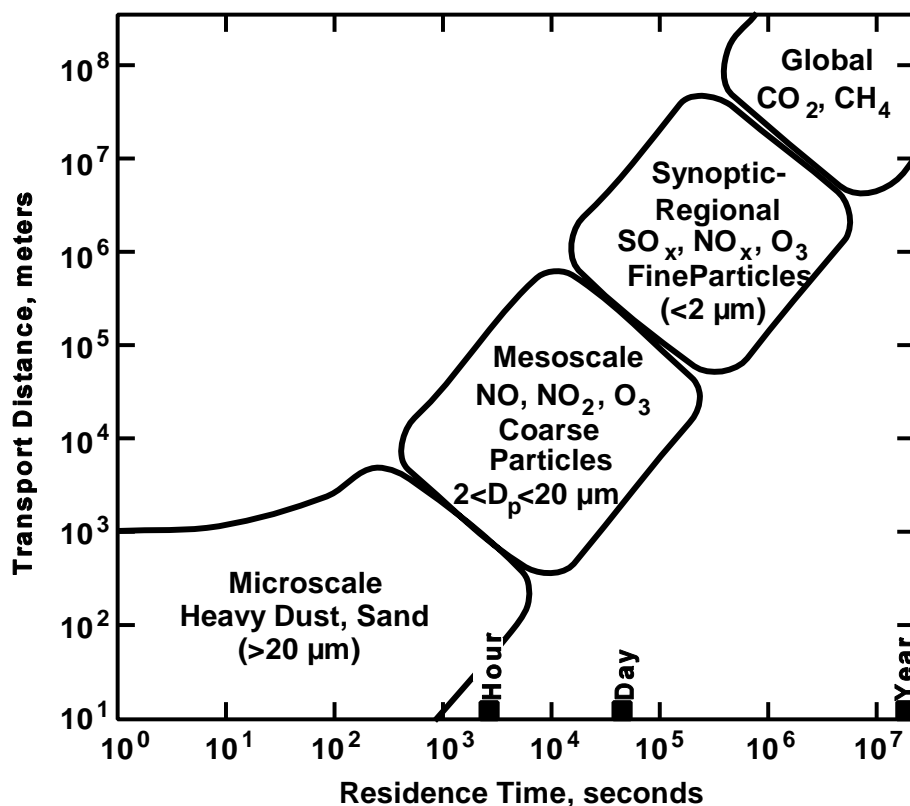
Figure 6-2.   Relationship of spatial and temporal scales for coarse and fine particles.

uniform regional patterns caused by long range transport. The relationship between spatial and temporal scales for coarse and fine particles is illustrated in Figure 6-2.

The aerosol residence time itself is determined by the competing rates of chemical transformations and removal. Secondary aerosol formation tends to be associated with multi-day long range transport because of the time delay necessary for the formation. For sulfates, for example, the residence time is 3-5 days. For fine particles, 0.1 μm to several μm, the main removal mechanism involves cloud processing, while coarse particles above 10 μm are deposited by sedimentation. Ultrafine particles, below 0.1 μm, also rapidly coagulate to form particles in the 0.1 to 1.0 μm size range. Another factor which must be considered is local turbulence. As a consequence of low removal rates, aerosols in the 0.1-1.0 μm size range reside in the atmosphere for longer periods than either smaller or larger particles (Figure 6-3).

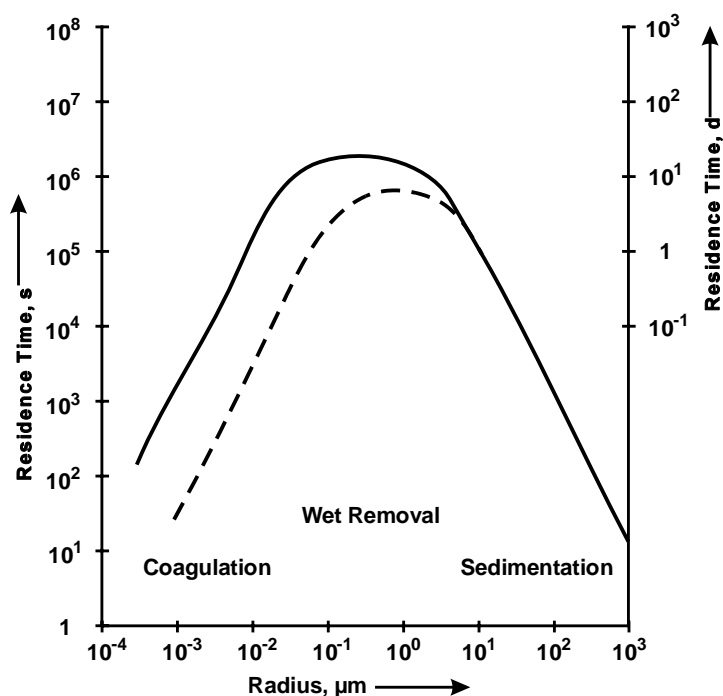**Figure 6-3.** **Residence time in the lower troposphere for atmospheric particles from 0.1 to 1.0 µm. (— Background aerosol, 300 particles cm^{-3}; --- continental aerosol, 15,000 particles cm^{-3}.)**

Source: Jaenicke (1980).

If aerosols are lifted into the mid- or upper-troposphere their residence time will increase to several weeks. Large scale aerosol injections into the stratosphere through volcanoes or deep convection result in atmospheric residences of a month or two months for ash and ≥ 2 years for sulfates formed from SO_2 oxidation.

In the context of the specific analysis that follows, the space-time-concentration relationship in urban and mountainous areas is of particular importance (Figure 6-4). Urban areas have strong spatial emission gradients and also may have corresponding concentration gradients for directly emitted species, particularly in the winter under poor horizontal and vertical transport conditions.

In mountainous regions, the strong concentration gradients are caused by both topography that limits transport as well as the prevalence of emissions in valley floors. Strong
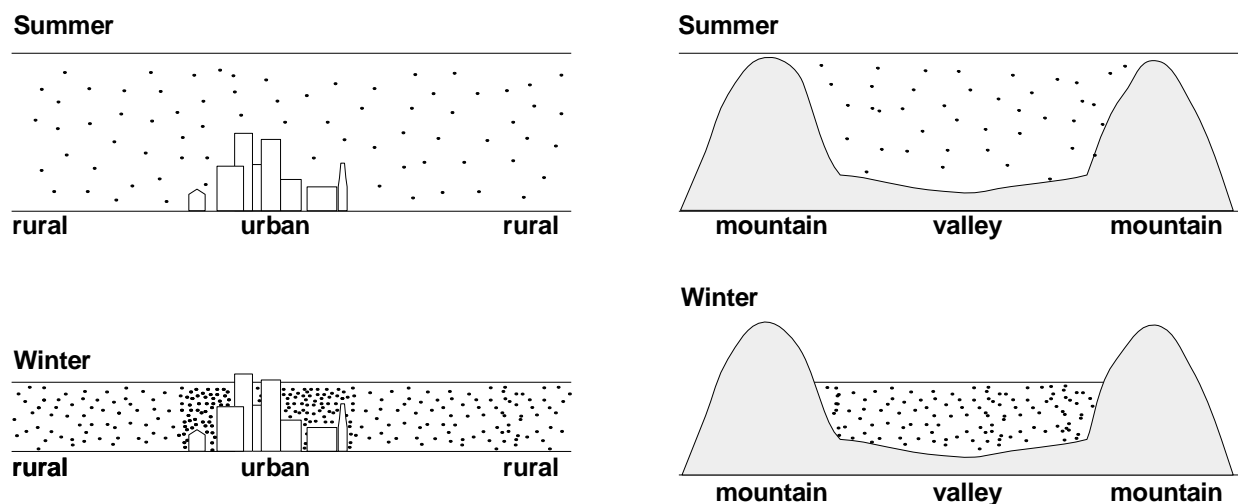
Figure 6-4.   Space-time relationship in urban and mountainous areas.

wintertime inversions tend to amplify the valley-mountain top concentration difference. Fog formation also accelerates the formation of aerosols in valleys

6.1.5   Particle Size Distribution

The aerosol size distribution is of importance in quantifying both the formation (generation) as well as the effects of aerosols. Condensation of gaseous substances during combustion in the atmosphere generally produces fine particles below 1 μm in diameter. Resuspension of soil dust and dispersion of sea spray produces coarse particles above 1 μm.

The size distribution of particles also influences both the atmospheric behavior and the effects of aerosols. Atmospheric coagulation, cloud scavenging, and removal by impaction and settling are strongly size dependent (Figure 6-3). The effects on human health depend on size-dependent lung penetration. The effects of light scattering on visibility and climate are also strongly dependent on particle size.

Measurements over the past decades (Whitby et al., 1972; Whitby, 1978) show that atmospheric aerosols may be classified as fine mode particles or coarse mode particles. The size distribution of atmospheric particles is discussed in Section 3.7. The sources, formation mechanisms, and chemical compositions of these two aerosol modes are different. In general,

the two aerosol size modes have independent spatial and temporal patterns as described throughout this chapter. Coarse dust particles tend to be more variable in space and time and can be suspended through natural or human activities. Fine particles during the warmer months of the year are largely of secondary origin and their spatial-temporal pattern is more regional. Notable exceptions are urban-industrial hotspots and mountain valleys where primary submicron size smoke particles can prevail.

6.1.6   Aerosol Chemical Composition

The chemical composition of atmospheric aerosol is believed to influence the effect on human health. While the causal mechanisms are not fully understood, the acidity, carcinogenicity, and other forms of toxicity are chemical properties considered relevant to human health.

The aerosol chemical composition has also become an important property for identifying source types based on chemical "fingerprints" in the ambient aerosol. Since aerosols reside in the atmosphere for days and weeks, there is a substantial amount of mixing that takes place among the contributions of many sources. At any given "receptor" location and time, the aerosol is a mixture of many source contributions each having a chemical signature for possible source type identification.

Fine particles are generally composed of sulfates, hydrogen ions, ammonium, organics, nitrates, elemental carbon (soot), as well as a portion of the trace metals (Section 6.6). Each major chemical form has sub-species such as acidic and neutral sulfates, light and heavy organics, ammonium and sodium nitrates, etc.

The chemical composition of coarse particles is dominated by the elements of the earth's crust, Si, Al, Fe, and other elements commonly found in soil. Near industrial sources, coarse particles may be contaminated by lead and other trace metals. At ocean shores, coarse particles may consist of sea salt arising from breaking of waves. Both resuspended dust and sea salt are primary particles, carrying the chemical signatures of their sources.

6.2   GLOBAL AND CONTINENTAL SCALE AEROSOL PATTERN

There are two data sets which can be used to provide information on fine particle concentration patterns on continental and global scales. Routine visibility distance observations, recorded hourly at many U.S. airports by the U.S. Weather Service, provide an indication of fine particle pollution over the United States. The visibility distance data have been converted to aerosol extinction coefficients and used to access patterns and trends of aerosol pollution over the United States (Husar et al., 1994; Husar and Wilson, 1993). Routine satellite monitoring of backscattered solar radiation over the oceans by the Advanced Very High Resolution Radiometer sensors on polar orbiting meteorological satellites provides a data set which can be used to give an indication of aerosol over the world's oceans. These two data sets have been merged to provide a global and continental perspective. The data analyses presented here were performed for this Criteria Document and have not yet been published elsewhere.

Aerosol detection over the oceans is facilitated by the fact that the ocean reflectance at 0.6 µm is only 0.02. Hence, even small backscattering from aerosols produces a measurable aerosol signal. The backscattering is converted to a vertically integrated equivalent aerosol optical thickness assuming a shape for the aerosol size distribution or phase function. Clouds are eliminated by a cloud mask, so the data are biased toward clear-sky conditions. The oceanic aerosol maps represent a two-year average (July 1989-June 1991) prior to the eruption of Mt. Pinatubo, when the stratosphere was unusually clear of aerosol. Consequently, the images reflect mainly the spatial pattern of tropospheric aerosol.

A continental-scale perspective for North America is shown in Figure 6-5. Seasonal depictions of the oceanic aerosol for the entire globe are shown in Figure 6-6. The average aerosol map of Eastern North America for June, July and August (Figure 6-5) shows areas of high optical depth over the Mid-Atlantic States and over the Atlantic Ocean. The aerosol concentration over the oceans is highest near the coast and declines with distance from the coast. This indicates that the aerosol is of continental origin and represents a plume originating in eastern North America, heading north-east across the Atlantic ocean. This plume can also be seen in the spring and summer season oceanic aerosol patterns shown in Figure 6-6.
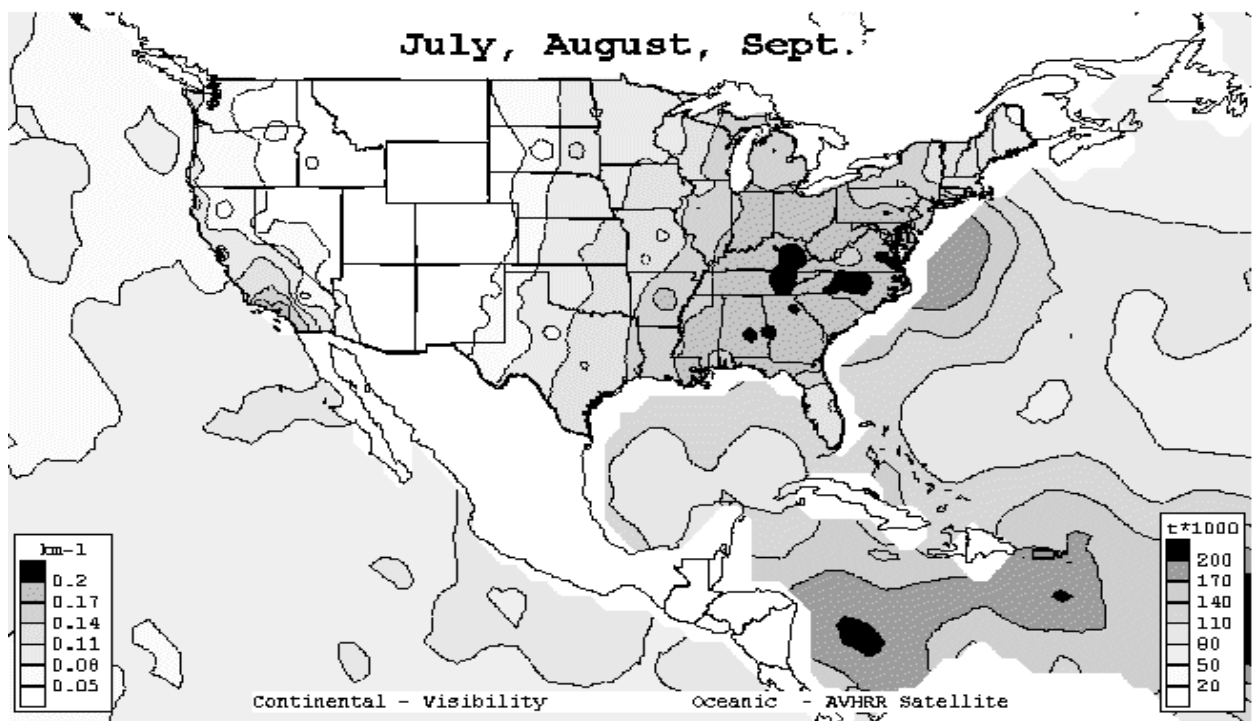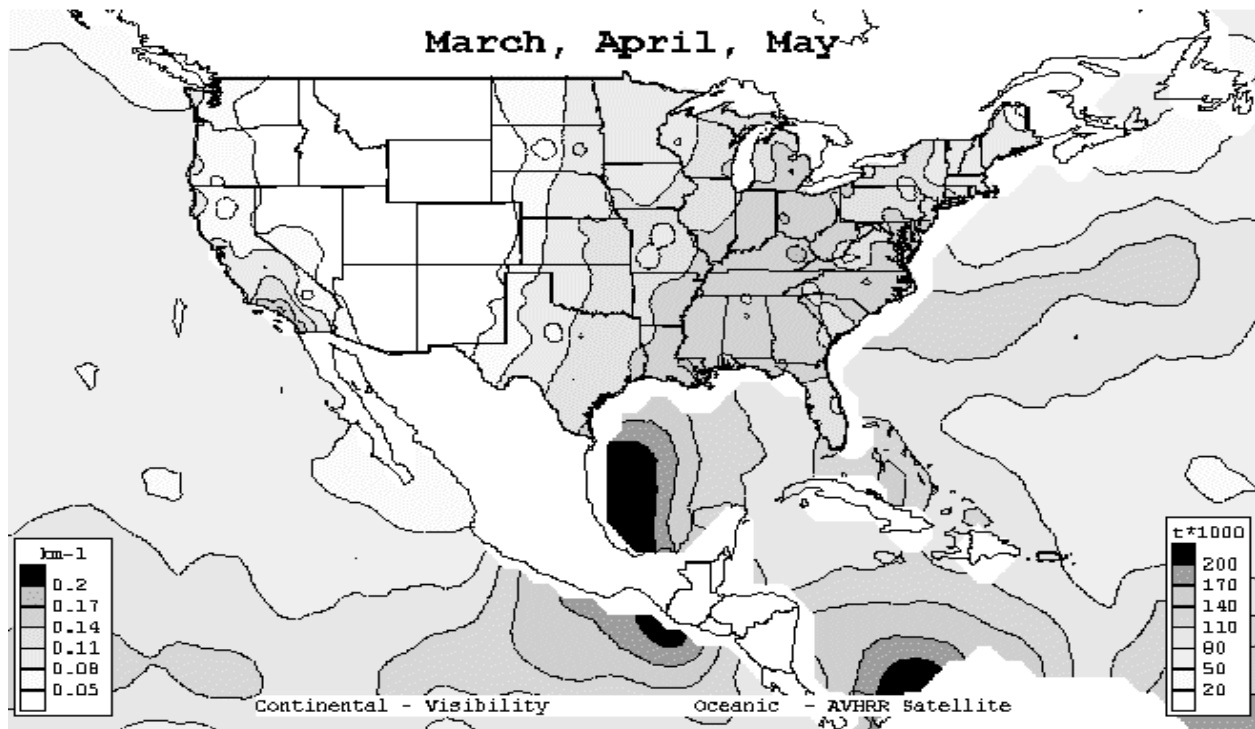
Figure 6-5. Continental scale pattern of aerosols derived from visibility observations over land and satellite monitoring over the oceans: North America.